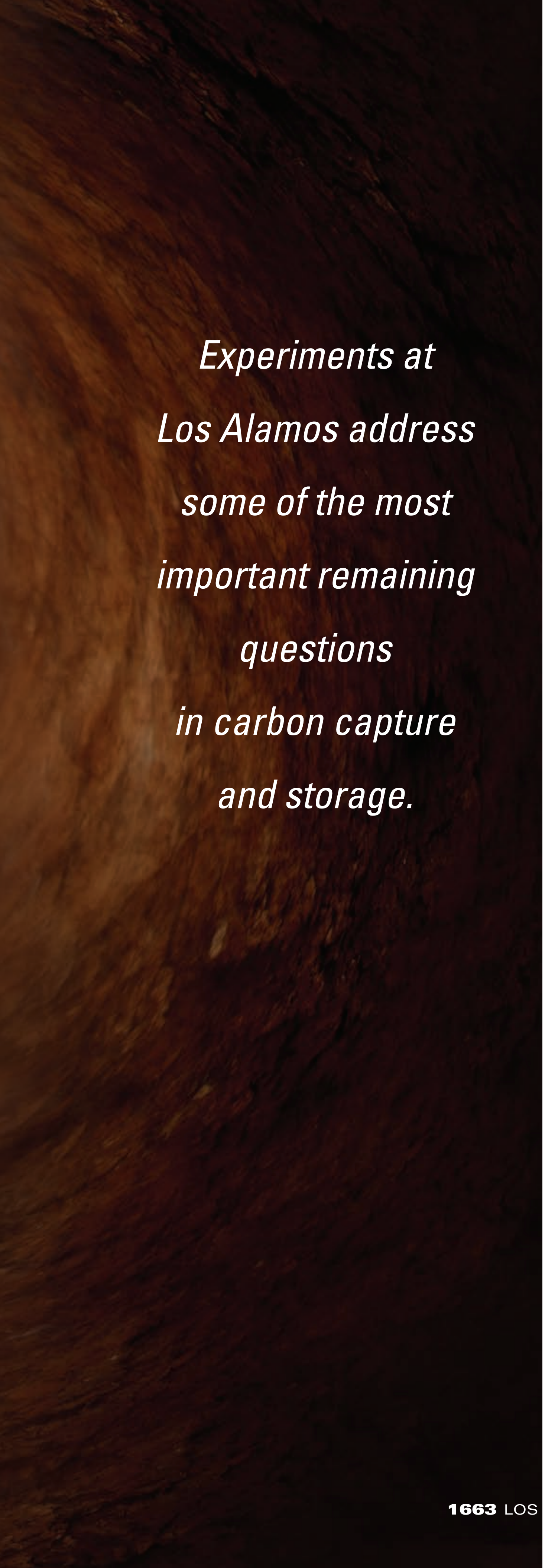
Putting Carbon Back where it came from

Most of the world's existing energy supply is stored underground in hydrocarbon fuels. The fuels are extracted and then burned, releasing carbon dioxide into the atmosphere and driving increasingly rapid climate change in the process. But a large-scale, international research program is working to overcome the remaining obstacles to putting that carbon back into the ground where it came from, and Los Alamos scientists are making significant progress on many fronts.



ADAPTING TO CLIMATE CHANGE WILL BE COSTLY. Severe weather events such as Superstorm Sandy, for example, result in huge costs for cleanup and repairs, and these events are increasingly associated with global climate change. As the climate warms due to the rising buildup of greenhouse gases in the atmosphere—primarily carbon dioxide (CO_2)—powerful storms continue to rack up public expense. And while it is impossible to attribute any particular storm to climate change, the increasing frequency and severity of storms is a predicted consequence of it.

Yet severe storms are just the tip of the melting iceberg. Rainforest, coastal, and wetland ecosystems are all at risk, as are the benefits they provide in terms of natural resources (food, wood, medicine) and services (water filtration, runoff control, carbon sequestration). In addition, any shift in water availability may threaten more frequent and more extreme droughts in some areas coupled with frequent and extreme floods in others. Wildfires, crop failures, and famine are possibilities. So, too, are malnutrition, water-borne illness, and the spread of infectious disease. All of this represents a steep price to be paid in lives and dollars.

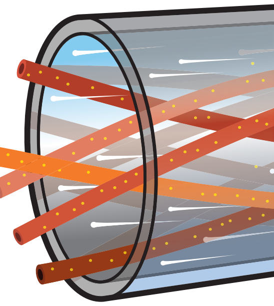
The primary human contribution to climate change is CO_2 emissions from fossil-fuel-based energy production. And for the foreseeable future, fossil fuels will remain the world's leading energy source because they are cheap and effective relative to renewables. Indeed, in the developing world, where the population increases are greatest, access to cheap energy is often considered critical to modernization. So mitigating the potential consequences of climate change depends on somehow reducing CO_2 output, yet the scale at which this must be done to offset human fossil fuel consumption is immense—posing a science and engineering challenge worthy of the national laboratories.

Deep Storage

Rajesh Pawar is the senior project leader of several Los Alamos partnerships working to test the feasibility of capturing most of the CO_2 produced by power plants and pumping it into geological storage reservoirs deep underground. Broadly referred to as carbon capture, utilization, and storage (CCUS), the effort aims to reduce the flow of CO_2 to the atmosphere. Pawar and his colleagues at Los Alamos, other national laboratories, and research sites around the world are working to create a commerically viable process in which, after the fossil fuels have been pulled out of the ground and consumed for energy, the residual carbon is properly put back where it came from.

Like any major energy-related undertaking—drilling for oil, burning coal, splitting atoms, or transmitting electricity—CCUS will involve some risk. Potential dangers include leaks and blowouts on the surface as well as groundwater impacts underground. These risks must be researched and understood in order to manage and minimize them in practice and develop technology to mitigate negative impacts. Safety and control systems must be designed, and the CCUS workforce must be trained to make sure the CO_2 stays where it belongs. That's why Pawar and others are busily investigating every facet of the problem before CCUS technology can be tested at a larger scale.

Although the nation's major initiative in CCUS has only been up and running in force for about 10 years, the oil and gas industry has been pumping pressurized CO_2 into underground oil reservoirs for enhanced oil recovery since the 1970s. The CO_2 acts to mobilize unrecovered oil, effectively making the oil easier to extract; this is, in fact, one type of utilization—the U in CCUS. Now, in order to reduce the amount of CO_2 entering the atmosphere, CCUS programs seek to pump supercritical CO_2—high-pressure, high-temperature CO_2 that expands to fill its container like a gas but can be pumped like a liquid—to a depth of more than a kilometer. The injected CO_2 will reside below drinking water aquifers in a porous rock layer. To take advantage of the same geological process that has long preserved oil and gas deposits in the subsurface, carbon storage reservoirs must have an impermeable caprock layer above the porous layer to prevent the buoyant CO_2 from migrating upward.



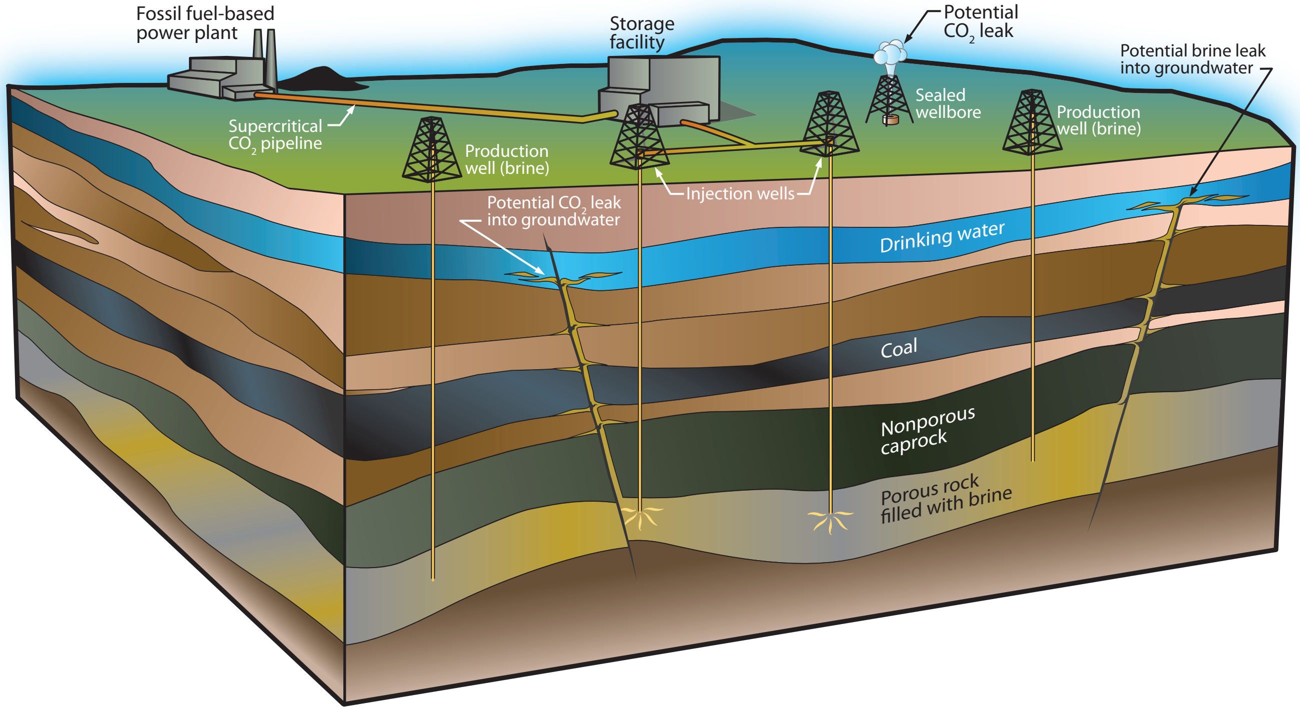
"One common misconception about carbon storage," says Pawar, "is that the underground storage reservoirs are empty, cavern-like structures. In fact, they consist of solid rock with tiny pores that are completely filled with salty, undrinkable water." Therefore, injected supercritical CO_2 must either displace the existing fluid—potentially requiring other deep wells to draw out the displaced salty water, called brine—or increase the subterranean pressure as more of the compressible, supercritical fluid is pumped into a finite space. In practice, both extracting brine and increasing pressure can occur in varying degrees. But because increased pressure poses challenges, including the potential to cause micro-earthquakes, the injection must be done with care. Fortunately, with time, some of the CO_2 will naturally dissolve into the brine, become trapped by capillary forces, or react with the rock, immobilizing the CO_2 and thereby reducing the pressure.

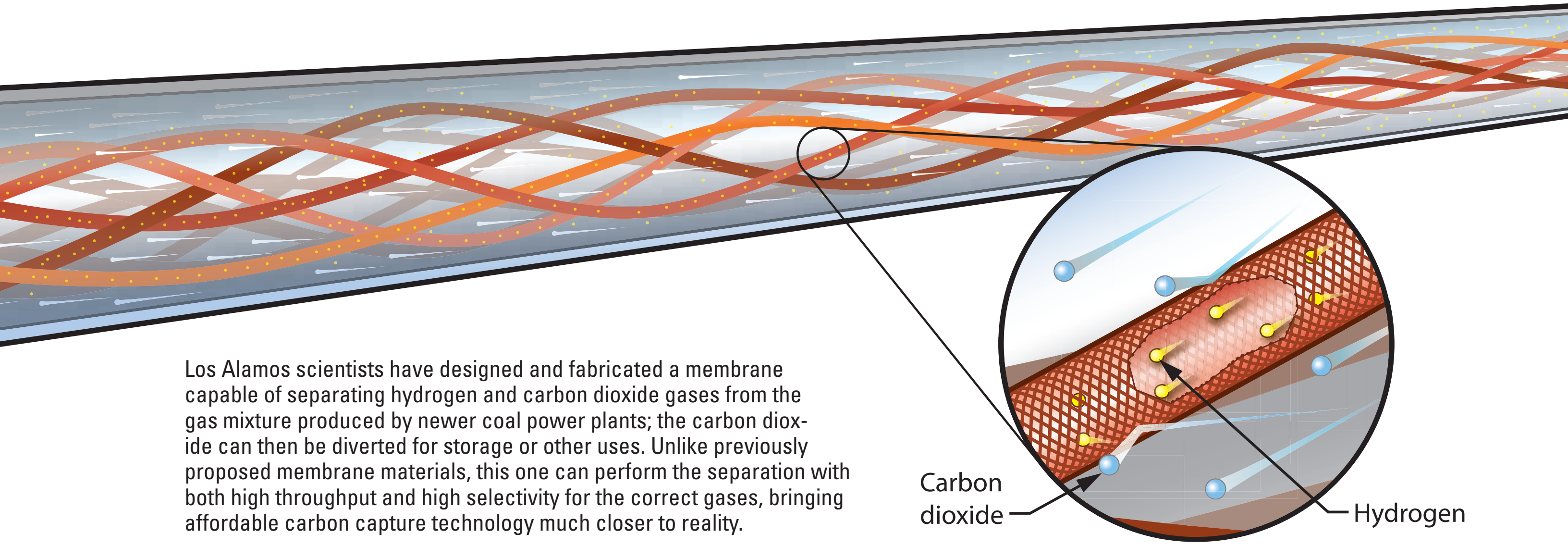
Infrastructure for CO_2 storage begins with a dedicated pipeline to transport supercritical CO_2 from the power plant, where the CO_2 must be captured, to the storage facility. There, injection wells (center) pump the CO_2 more than a kilometer underground to a porous rock layer containing salty water known as brine. Above this injection layer lies a wide, nonporous caprock layer to keep the CO_2 mixture in place in spite of its natural buoyancy—the same geological mechanism that keeps pressurized oil and gas reservoirs intact. To alleviate the pressure increase caused by the injection of CO_2, multiple production wells (left and right) may extract hot brine from the deep reservoir, providing a potential source of both geothermal energy and industrially usable water.

As with other large-scale energy applications, the carbon storage facility must be managed to prevent potential problems. In particular, its operators must continually monitor the field for evidence of CO_2 escaping from its storage reservoir. This can happen if defects in the rock layers create an upward migration path. Such defects can occur along geological faults (diagonal lines) or wellbores, and any migrating CO_2 might end up in two places of concern: drinking water reservoirs and the atmosphere. Similarly, brine might migrate along the same defect paths up to a drinking water layer, bringing with it salt and potentially harmful heavy metal contaminants.

Comprehensive monitoring to keep abreast of any such migration includes seismic imaging of the underground storage reservoir; direct sampling from key underground sites closer to the surface, including along well bores and in drinking water reservoirs; and sensor-based scanning across the surface for elevated CO_2 levels. Experience to date demonstrates that leaks to the surface are rare and can be detected early and corrected.

Los Alamos research has led to significant improvements to virtually every aspect of this complex, multifaceted effort: more efficient CO_2 capture at the power plant, better understanding of the potential for groundwater contamination by CO_2 or brine (including which sites are likely to avoid the problem and under what conditions it might naturally resolve itself), sealing off retired well bores such that any microscopic defects will exhibit self-healing, detecting evidence of stored CO_2 migration against a background of natural CO_2 sources, and analyzing potential storage sites for geological and economic suitability.





Los Alamos scientists have designed and fabricated a membrane capable of separating hydrogen and carbon dioxide gases from the gas mixture produced by newer coal power plants; the carbon dioxide can then be diverted for storage or other uses. Unlike previously proposed membrane materials, this one can perform the separation with both high throughput and high selectivity for the correct gases, bringing affordable carbon capture technology much closer to reality.

However, the ability to successfully manage underground storage depends not only on the quantity and pressure of the material to be stored, but also on the duration. Ideally, if the material could be stored for hundreds of thousands of years, it would have time for slow reactions with the surrounding rock that result in solid carbonate minerals, which could remain there indefinitely, unsupervised. But the technical challenge of ensuring such a long storage period borders on the impractical. On the other hand, if the storage period is too brief, the world won't have enough time to switch to alternative energy sources that don't produce CO_2. Experts and policy makers have, therefore, decided to target an intermediate time scale of approximately 1000 years. As the thinking goes, if the stored CO_2 leaks slowly over this time period, it won't be terribly damaging because the world will be shifting away from burning fossil fuels. (Presumably, humankind will have succeeded in switching to carbon-free energy sources during those 1000 years due to advances in technology—and because the world's supply of fossil fuels is finite.)

Making a Dent

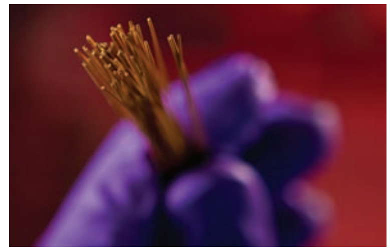
According to the Environmental Protection Agency, current annual CO_2 emissions in the United States are about six billion tonnes (metric tons: 1000 kg or 2205 lbs) out of about 30 billion tonnes worldwide. In order to contribute substantially to the solution, CCUS technology will eventually need to remove one billion tonnes of CO_2 per year worldwide. That would involve retrofitting existing power plants with carbon capture technology, building new plants with integrated capture technology, and constructing new pipelines to transport a volume of liquid CO_2 equal to about 35 percent of the world's oil production.

Still, with coal and other fossil fuel plants projected to continue to provide the majority of humanity's energy consumption for at least another 20 years, experts at Los Alamos and elsewhere are working to make CCUS as safe and economical as possible. A handful of existing CCUS pilot programs currently capture and store on the order of a million (not billion) tonnes of CO_2 per year, and a number of larger, industrial-scale CCUS projects are expected to be in operation in the United States and elsewhere by 2020. Then, in order to practically scale the collective tonnage up from millions to billions, three things will need to happen: larger geological repositories will need to be identified and tested, new pipelines and other infrastructure will need to be built, and the additional expense incurred due to CCUS activity per watt of energy produced will need to come way down. Finding suitable repositories may not be overly problematic, as deep saline aquifers are quite common and have an estimated worldwide capacity of ten *trillion* tonnes of CO_2. But reducing per-watt costs has proved significantly more challenging: the DOE target calls for 90 percent of all CO_2 generated by coal-based power production to be captured and stored at a maximum increase to the cost of electricity of 35 percent (for the least efficient existing power plants) and 10 percent (for newer, more efficient plants). Pilot programs don't even come close—not yet, anyway.

Creative Capture

Of all the CCUS activities—capture at the power plant, compression into fluid, transportation in pipelines, and underground injection and management—existing capture technologies account for upwards of 75 percent of the total expense. That capture expense is particularly large for our oldest, lowest-tech power plants, which require post-combustion carbon capture: the CO_2 must be separated and compressed from the plant's low-concentration, low-pressure exhaust gas—an energy intensive process. And the U.S. Energy Information Administration estimates that by 2030,

(Left) Kathryn Berchtold, team leader for Carbon Capture and Separations for Energy Applications at Los Alamos, and postdoctoral researcher Ganpat Dahe examine the hollow fiber membranes that she believes will ultimately be bundled into a commercially viable carbon capture module. (Below) Hollow fiber membranes for gas separation.



the current fleet of post-combustion power plants will still be responsible for 78 percent of the country's CO_2 emissions from electricity generation. Reducing capture costs at such plants constitutes the tremendous technological challenge facing Los Alamos's CaSEA team (carbon capture and separations for energy applications), led by Kathryn Berchtold.

Berchtold and her CaSEA colleague Rajinder Singh have been developing and experimenting with promising new membrane materials for inexpensively separating CO_2 from coal-derived gas streams produced during power generation processes. They aim to design, demonstrate, and ultimately commercialize a membrane-based separation process for both existing and next-generation power plants. That means identifying the best materials for the job and then maximizing throughput by laying those materials down in as thin a layer as possible without sacrificing structural integrity—hundreds of times thinner than a human hair. To that end, Berchtold and Singh have developed a novel ultrasonic atomization technology for depositing CO_2-selective layers onto a commercially viable, porous polymer film, which could then be rolled up for packaging and use. CaSEA scientists believe that the adaptability of this method will allow it to make that rare, but all-important, transition from the laboratory benchtop to real-world industrial use.

The CaSEA team is also pursuing separations technologies that meet the needs of more efficient, next-generation power plants. In these plants, a coal gasifier produces syngas: a mixture of hydrogen (H_2) and carbon monoxide (CO), plus other trace gases. The syngas is then reacted with steam, converting the CO to CO_2 while producing additional H_2. The H_2 is then separated from this mixed gas stream prior to its combustion. It burns cleanly and can be used as a transportation fuel or a source of electricity. All that remains is to compress the waste CO_2 and send it off to be injected deep underground.

One technology under development by the CaSEA team to separate H_2 from CO_2 comprises a special membrane material based on a commercially available chemical called polybenzimidazole (PBI) deposited on hollow-fiber support structures. These PBI-coated hollow fibers—roughly the diameter of a human hair—selectively allow the smaller H_2 molecules to pass into the hollow fibers while blocking the larger CO_2 molecules. Pressure and concentration gradients drive the separation.

"What's amazing about this PBI-based polymer is that it's stable at temperatures where most other polymers would degrade," Berchtold says. "This is a must for use at high gasification process temperatures. Matching the process and separation temperatures with a technology that's durable under those conditions is key to minimizing the cost of carbon capture." Indeed, the team's materials have proven extremely durable, outperforming all the other organic membranes identified for separating the syngas-derived mixture. Such membranes generally suffer from a trade-off: the better they are at distinguishing between the two gases, the lower their overall throughput. But the new PBI membrane shows a simultaneous improvement on both counts, and, as a consequence, Berchtold believes it finally puts the DOE's goal of capturing 90 percent of the CO_2 at only 10 percent increased cost of electricity within reach.

Heavy Metals in Concert

Back on the storage side, Los Alamos hydrogeologist Elizabeth Keating is asking a tough question: Could leakage of CO_2 from deep underground storage migrate upward, perhaps along undetected geologic faults or in leaking wells, and contaminate shallow-aquifer drinking water? Famous examples in France (where Perrier is bottled) show that carbonated water is not necessarily harmful. However, CO_2 may, in some circumstances, cause rocks in the aquifer to release toxic heavy metals into the drinking water. In addition, pressure in the storage reservoir may drive brine that contains heavy metals upward into the groundwater. These potentialities must be prevented, and that may not be easy.

Keating studies the CO_2-bearing groundwater at field sites she considers to be natural analogs to a leaking, large-scale carbon storage repository—sites where nature has provided migrating CO_2 within the geological strata through volcanic or other tectonic activity. (Sites of this sort would not be chosen for carbon storage operations.) One such site is just a 30-minute drive from Los Alamos, in Chimayó, New Mexico, where some locations have groundwater quality problems: the toxic elements arsenic and uranium are naturally present in the water. Keating samples groundwater and sediments over time for use in laboratory experiments, materials characterization, and computational modeling to determine how the natural CO_2 springs might contribute to the groundwater quality problems. She finds that brine accompanying the CO_2 as it rises from depth contains arsenic and uranium, while CO_2 reactions with aquifer rocks do not play an important role in releasing these elements.

"Because arsenic and uranium are strongly correlated with salinity at some of the wells," Keating says, "it's much more likely that brine from deep below, which is already rich in these metals, is coming up in those spots, too." If CO_2 storage operations cause a similar effect, it could become a deal-breaker for CCUS in general. Yet at other field sites, groundwater has proven to be well isolated from brine intrusion. Keating's research at a site in Springerville, Arizona, where CO_2 naturally enters the groundwater but metal-laden brine does not, may help identify why some locations are susceptible to brine entering shallow aquifers but not others.

Even without brine intrusion, what prevents CO_2 reactions with aquifer rocks from introducing toxic metals into the drinking water? Research at Chimayó by Keating and colleagues reveals an answer: minerals in the aquifer, such as iron-bearing clays, naturally draw the metals out of solution. This likely explains the absence of detectably elevated concentrations of arsenic or uranium in lower-salinity wells. It is not clear how quickly this process would remove toxic metals if a CO_2 storage reservoir were to leak, however, making further research essential.

To Seal the Deal

Of course, there is another concern, apart from groundwater contamination, associated with upward displacement from carbon storage sites. What if the CO_2 leaks back into the atmosphere? A large release could be life-threatening, displacing breathable oxygen from the air, but even a steady leak at nontoxic concentrations could undermine the purpose of the storage effort. Is there any way to verify that the captured gas won't just find its way out of the ground during its thousand years of intended containment?

Los Alamos scientists Dennis Newell and Bill Carey are trying to demonstrate just that. They argue that one of the most likely places to spout a significant leak is actually at the wellbores themselves. Whether designed for injection of CO_2, production of brine, or oil and gas operations, wellbores are plugged with cement across the deep caprock to isolate the CO_2 (or oil or gas) below from the groundwater above it and the surface. Even though many energy scientists expect that CO_2 injection will be a temporary measure—just until non-fossil-fuel energy sources can be widely deployed in 100 years, perhaps—the carbon must stay stored long after that, beneath a large number of sealed-off wellbores.

Newell and Carey recently performed a series of laboratory experiments designed to test wellbore seal integrity. They built a test seal between siltstone and cement to simulate a sealed wellbore but deliberately included a defect between the two layers. They then flooded it with a

(Left) The Arenal volcano in Costa Rica is an extreme example of a natural analog to a carbon storage site in which the CO_2 migrates upward to the surface. (Right) Los Alamos hydrogeologist Elizabeth Keating stands by a somewhat less dramatic natural analog, where underlying CO_2 ascends to the groundwater and the atmosphere at her field site in Chimayó, New Mexico.

CREDIT: (RIGHT) DANIEL LEVITT/LANL

high-temperature, high-pressure mixture of brine and supercritical CO_2 and measured the seal's permeability over time. Remarkably, that permeability decreased threefold over a period of days without any interference from the scientists.

"Based on our research, nature may be able to help with some of our problems," Newell says. "You've got a major leakage pathway in a mile-deep, manmade hole, and under some conditions, it actually heals itself. It is very important for us to identify the situations where self-healing can occur and those where it is unlikely." Detailed microscopic analysis revealed reactions of CO_2 with cement, showing where the brine-CO_2 fluid had migrated along the defect. Further evaluation of those penetration sites revealed that cement in the defect zone had been altered by the brine-CO_2 fluid and redeposited farther along in the defect, obstructing the leak.

For Carey, this is a gratifying result, because years of field-site leak testing have shown him that the cement interfaces are the most vulnerable parts of wellbore systems. If the self-healing behavior is found to be universal, or perhaps even inducible, he believes this will go a long way toward securing carbon storage reservoirs—an important step in making CCUS a reality.

The 2010 Deepwater Horizon oil spill in the Gulf of Mexico is perhaps the best-known example of a wellbore failure—a phenomenon that Los Alamos scientists actively research in the context of keeping geologically stored CO_2 in the deep underground reservoirs where it was injected.

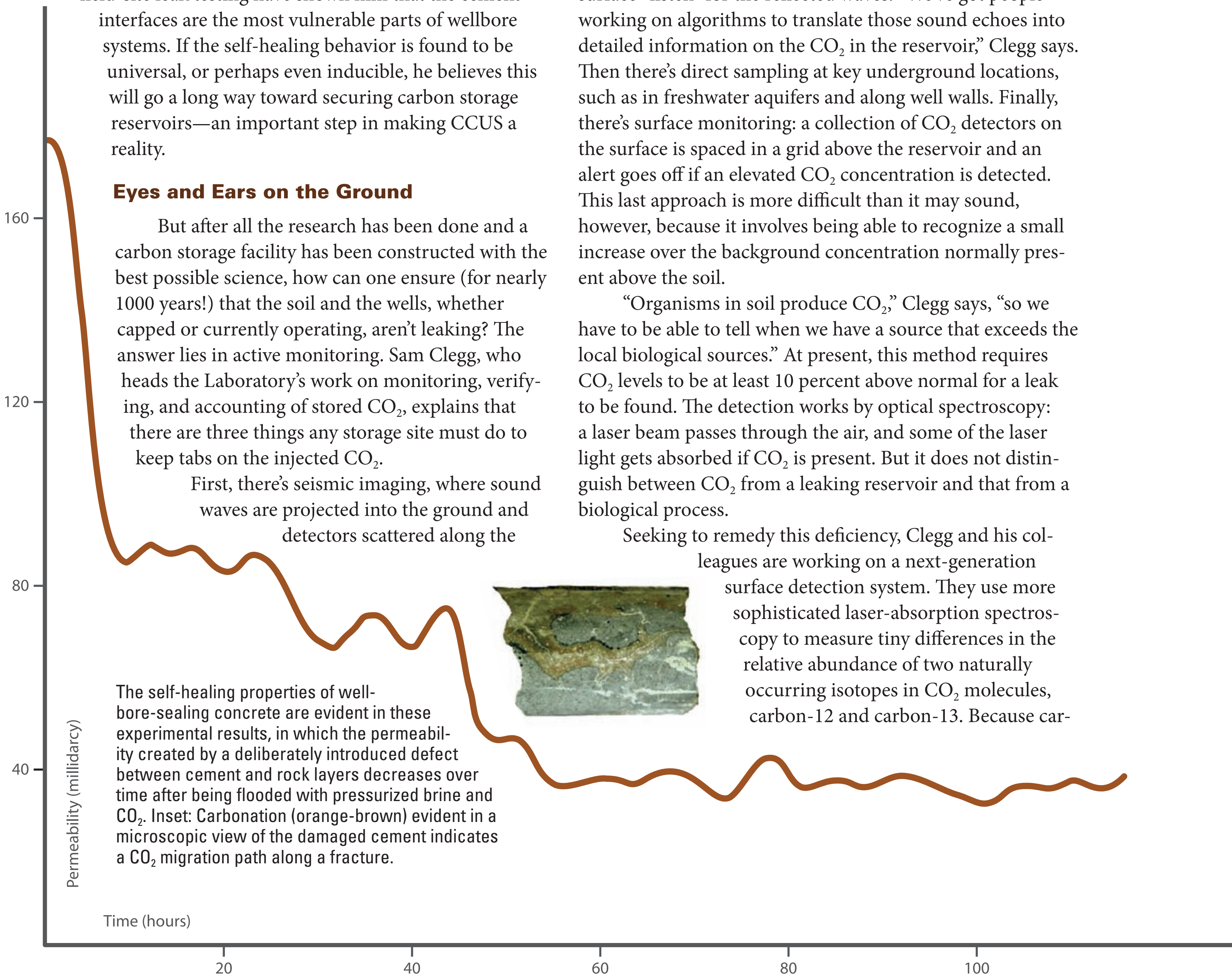
Eyes and Ears on the Ground

But after all the research has been done and a carbon storage facility has been constructed with the best possible science, how can one ensure (for nearly 1000 years!) that the soil and the wells, whether capped or currently operating, aren't leaking? The answer lies in active monitoring. Sam Clegg, who heads the Laboratory's work on monitoring, verifying, and accounting of stored CO_2, explains that there are three things any storage site must do to keep tabs on the injected CO_2.

First, there's seismic imaging, where sound waves are projected into the ground and detectors scattered along the surface "listen" for the reflected waves. "We've got people working on algorithms to translate those sound echoes into detailed information on the CO_2 in the reservoir," Clegg says. Then there's direct sampling at key underground locations, such as in freshwater aquifers and along well walls. Finally, there's surface monitoring: a collection of CO_2 detectors on the surface is spaced in a grid above the reservoir and an alert goes off if an elevated CO_2 concentration is detected. This last approach is more difficult than it may sound, however, because it involves being able to recognize a small increase over the background concentration normally present above the soil.

"Organisms in soil produce CO_2," Clegg says, "so we have to be able to tell when we have a source that exceeds the local biological sources." At present, this method requires CO_2 levels to be at least 10 percent above normal for a leak to be found. The detection works by optical spectroscopy: a laser beam passes through the air, and some of the laser light gets absorbed if CO_2 is present. But it does not distinguish between CO_2 from a leaking reservoir and that from a biological process.

Seeking to remedy this deficiency, Clegg and his colleagues are working on a next-generation surface detection system. They use more sophisticated laser-absorption spectroscopy to measure tiny differences in the relative abundance of two naturally occurring isotopes in CO_2 molecules, carbon-12 and carbon-13. Because car-



The self-healing properties of wellbore-sealing concrete are evident in these experimental results, in which the permeability created by a deliberately introduced defect between cement and rock layers decreases over time after being flooded with pressurized brine and CO_2. Inset: Carbonation (orange-brown) evident in a microscopic view of the damaged cement indicates a CO_2 migration path along a fracture.

bon-13 is heavier than carbon-12, it is used a little differently in chemical processes, manmade or otherwise. That difference is exaggerated in CO_2 produced by the burning of fossil fuels, producing a significant deficit in carbon-13 relative to that in CO_2 of biological origin. Together with seismic imaging and underground sampling, this surface detection system should eliminate the possibility of a leak going undetected.

Uplifting Prospects

Finding and exploring prospective storage sites is another research-intensive part of the CCUS initiative, and that's where Phil Stauffer, a Los Alamos hydrogeologist, comes in. Together with colleagues at the Laboratory and collaborators from the University of Wyoming, Stauffer has developed detailed computer simulations of a proposed CO_2 storage facility on the Rock Springs Uplift in southwestern Wyoming. The site has deep, porous limestone and sandstone layers amenable to carbon storage and is proximate to a coal-fired power plant that produces 18 million tonnes of CO_2 annually. The simulations show 50 years at 80 percent injection from the power plant (15 million tonnes per year) with minimal leakage into the caprock above and projected additional storage capacity for well over a century from all of the large CO_2-producing operations in southwestern Wyoming, amounting to about 30 million tonnes annually, roughly half of the state's total carbon emissions.

"We have new, high-resolution, 3-D seismic data that allows us to vastly improve our geologic models," Stauffer says. Together with a deep test well, a long core sample, and other sampling and analysis components, the new, data-rich simulation may allow the proposed facility to come to fruition. "We have transitioned from an idealistic, generalized assessment of the storage site to a realistic, low-risk assessment—one that finally justifies the investment to begin constructing a commercial storage operation."

Initially, the Rock Springs Uplift storage facility would span 100 square miles on the surface, requiring 26 injection wells and at least as many production wells, which make room for the injected supercritical fluid by drawing out the existing brine. These production wells are important because they reduce the pressure in the deep aquifer. This dramatically reduces the likelihood of excessive leaking, either upward or sideways beyond the footprint of the facility. It also significantly reduces the danger of triggering earthquakes due to overpressure, which could then lead to increased leakage. (Earthquakes have led to the cancellation of subsurface geothermal injection projects in Europe and the United States.)

A second benefit of extracting brine may come from the brine itself. During 50 simulated years of operation, approximately one cubic kilometer of simulated CO_2 was injected, resulting in about a cubic kilometer of simulated brine being produced. The large volume of very salty water, more than twice as salty as seawater, comes out of the ground at temperatures exceeding 100°C, making it a potentially useful source of geothermal energy. Additionally, the water could be desalinated for industrial or agricultural applications (if not for drinking), provided that the economic value of the produced freshwater justifies the expense of desalination. However, if desalination is not economically feasible, then proper disposal of the brine may prove difficult and expensive.

Stauffer's calculations make reasonable assumptions about well installation and operation costs. The proposed facility, he finds, would add only about one dollar to the cost of energy production per tonne of stored CO_2—a miniscule fraction of the cost of capturing the CO_2 from the power plant's exhaust to begin with.

Whether the Rock Springs Uplift plant goes forward or not, the DOE appears to be keeping up with its current timeline for developing and deploying CCUS technology. If surface and groundwater safety can be better assured and cost objectives met, then one or more full-scale demonstration facilities can begin on schedule in 2020. From there it will be a matter of improving the cost efficiency of capture technologies and scaling up overall deployment to the level where CCUS can make a serious dent in the emissions driving climate change.

With such a grand objective looming so near in the future, one might expect Rajesh Pawar and his colleagues around the country to feel a restless apprehension with every day that goes by. But in the wake of recent CCUS discoveries and achievements from Los Alamos, Pawar expresses optimism that the comprehensive effort to master this complex, new science can proceed as planned.

"Success in CCUS is all about removing the uncertainties," Pawar says, "and that's exactly what these projects are doing." ❖ LDRD

—Craig Tyler

The Jim Bridger coal-fired power plant lies on Southwestern Wyoming's Rock Springs Uplift, a promising site for a CO_2 storage operation.